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## Structural effect of heavy ion irradiation on GdBaCuO ceramics

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**Résumé.** — Nous avons irradiés des cristaux GdBaCuO avec des ions Kr de 480 keV à 40 et 300 K. L'évolution d'un cristal présentant une structure monoclinique voisine de la structure orthorhombique a montré qu'une petite déformation initiale du réseau n'a pas d'influence sur les défauts étendus induits par irradiation. Nous avons mis en évidence le rôle de puits des joints de macles sur les défauts créés. Un film vidéo montre en effet l'interaction dynamique des dislocations avec les joints de macles. Une amorphisation progressive est ensuite observée pour des doses  $> 4 - 5 \times 10^{12}$  Kr/cm<sup>2</sup>. Dans tous les cas une occasionnelle transition vers la structure tétragonale n'apparaît qu'après le début de l'amorphisation.

**Abstract.** — The influence of twin boundaries as sinks on defects induced by 480 keV Kr ion irradiation in GdBaCuO crystals was observed *in situ* at 40 and 300 K. The interaction of the dislocations with the twin boundaries followed on a video recording. A crystalline to amorphous transition was observed above a total fluence of  $\sim 4 - 5 \times 10^{12}$  Kr/cm<sup>2</sup>. A comparison between orthorhombic (Os) crystals and a monoclinic structure (Ms) (close to Os and whose parameters were calculated) shows that the behaviour of irradiation-induced extended defects does not depend on a small initial deformation of the orthorhombic cell. In both case, an occasional orthorhombic (or monoclinic) to tetragonal phase transition only occurs when the amorphization process has begun.

Ion irradiation studies of the high  $T_c$  superconductors are providing increasingly interesting information on their structural stability (e.g. [1-8]. The controlled introduction of defects may also lead to important applications [9-11]. Understanding the nature of these defects, their evolution and their relation to structural and electronic property changes

Structural studies related to electrical investigations with various radiation fields (e.g. 120 keV to 1 MeV electrons [3, 6, 12, 13], 50 to 300 keV He ions [2, 14], or 400 to 2 MeV O ions [1, 15, 16]) have demonstrated that with the possible exception of GeV-ion irradiations [17], irradiation by different ions at varying energies, produced essentially identical effects on the superconducting critical temperature  $T_c$ , the critical current  $J_c$  or on the normal conductivity as long as the displacement per atom (dpa) ratio was the same. An orthorhombic to

tetragonal (OTT) transition occurs due to a local oxygen disordering and then, at a level 5 to 10 times higher, amorphization occurs due to cation disordering [2, 7]. This was true, at least, as long as the deposited energy density (i.e. the instantaneous concentration of displaced atoms along the incident ion trajectory) remained comparatively low such as for MeV Ar<sup>+</sup> or keV He<sup>+</sup> 18.

In this paper we show dynamical transmission electron microscopy (TEM) observations of the irradiation-induced defect evolution in GdBaCuO crystals under heavy ion irradiation (Kr ions at 480 keV). Such heavy ions produce high deposited energy densities in an individual cascade and hence large localized defect concentrations. This leads to dislocation (or dislocation loop) formation as well as visible clusters creation (yield  $\leq 0.1$ , mean size  $\sim 10$  to 20 nm). As the cluster density increases, amorphization progressively occurs (threshold flu-

ence  $\geq 9 \times 10^{12}$  Kr/cm<sup>2</sup>). Occasionally we observed in parallel an orthorhombic to tetragonal (OTT) transition (no phase transition was observed below the amorphization threshold dose). A second important point is the high mobility of the irradiation induced defects which gives rise to a spectacular interaction with the twin boundaries at 40 K as well as at room temperature. This effect, observed for the first time to our knowledge, leads to both the dislocation motion and twin boundary deformation.

All these observations are still valid in the case of a monoclinic structure (Ms) corresponding to a deformation of the basic orthorhombic (Os) lattice. The lattice parameters are calculated and some information relative to the space group of the monoclinic structure are obtained.

### Experimental.

**1. SAMPLE CHARACTERISATION.** — Small GdBaCuO single superconductor crystals [19, 20] were crushed and deposited on carbon-coated grids for microscopy investigations. Some of the deposited small crystals exhibit a monoclinic structure (Ms) close to the Os. The determination of this structure is reported below. In this work we mainly followed the structural evolution at 40 and 300 K of Os crystals with the *c* axis both perpendicular and parallel to the free surfaces which exhibit twin boundaries. At 40 K a monoclinic crystal was also studied.

**2. IRRADIATION CONDITIONS.** — The 480 keV Kr ion irradiations were performed *in situ* in a Philips EM400 electron microscope on line with the ion implantor [21]. We have used a standard double tilt sample holder for the 300 K irradiation and a custom-built single-tilt helium-cooled sample holder [22] for the 40 K investigations. To avoid a sample temperature increase during irradiation, the dose rate was kept down to  $\sim 2 - 4 \times 10^9$  Kr cm<sup>-2</sup> s<sup>-1</sup>. The maximum fluence reached was  $2.5 \times 10^{13}$  Kr/cm<sup>2</sup>, so that even the maximum fluence only leads to a Kr doping level of a few ppm in the matrix and the induced damage is essentially due to irradiation effects.

### Results.

**1. MONOCLINIC STRUCTURE DETERMINATION.** — Electron diffraction patterns (EDP) taken prior to irradiation show a deformed  $[1\bar{1}1]$  zone axis of the Os structure (i.e. the angle between the  $(\bar{1}01)$  and  $(011)$  directions is not 90° but 86.5° (Fig. 1)). From such pattern we deduced a monoclinic structure with the following parameters  $a_m = 0.403 \pm 0.02$  nm,  $b_m = 0.384 \pm 0.002$  nm,  $c_m = 2.350 \pm 0.05$  nm and  $\beta = 75^\circ \pm 1^\circ$ . Comparing with the orthorhombic

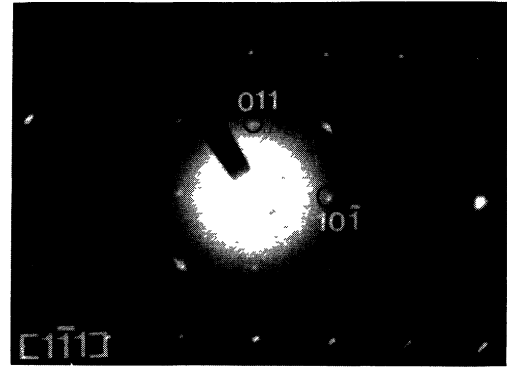


Fig. 1. — EDP from a GdBaCuO crystal showing a monoclinic structure ( $[1\bar{1}1]$  zone axis).

parameters the corresponding ratios are  $a_m/b_{Os} = 1.055$ ,  $b_m \cong a_{Os}$ ,  $c_m \sim 2 c_{Os}$ . The interplanar distances between Os and Ms structures are close :

$$\begin{aligned} (100)_m, (006)_m \sim (010)_{Os}, (003)_{Os} &\cong 0.387 \text{ nm}, \\ (010)_m \sim (100)_{Os} &\cong 0.382 \text{ nm} \\ \text{and } (110)_m \sim (110)_{Os} &\cong 0.273 \text{ nm}. \end{aligned}$$

During irradiation an apparent deformation/rotation of this structure leads to the observation of three successive zone axes (Fig. 2)  $[\bar{5}21]$ ,  $[1\bar{2}1]$  and  $[41\bar{1}]$  (respectively above  $\sim 3 \times 10^{11}$ ,  $1.2 \times 10^{13}$  and  $1.7 \times 10^{13}$  Kr/cm<sup>2</sup>). These zone axes were indexed according to the Ms structure parameters found above. We specifically checked that

$$\begin{aligned} \langle (0\bar{1}2), (105) \rangle &= 86.5^\circ, \quad \langle (\bar{1}01), (012) \rangle = 84^\circ \\ \text{and } \langle (011), (104) \rangle &= 83.5^\circ. \end{aligned}$$

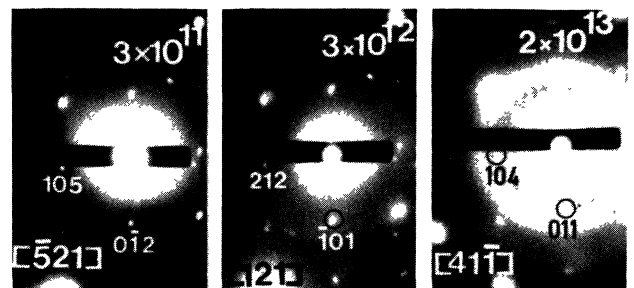


Fig. 2. — Same crystal as in figure 1 during 480 keV Kr ion irradiation. EDP showing different zone axes (see text).

As crystal thickness varies through the area studied, little information can be obtained from the spot intensities. In addition no ring pattern from a polycrystalline area is available, so that the missing planes cannot be determined. This does not allow an unambiguous determination of the (Ms) space group. Nevertheless, from the four zone axes some

rules can be deduced (e.g. reflexions are allowed for  $(hhl)$  with  $l$  odd,  $(\bar{h}hl)$  with  $l$  even,  $(h0l)$  and  $(hk0)$  with  $h$  odd and  $(0kl)$  with  $k$  odd).

**2. DEFECT EVOLUTION.** — At both 40 and 300 K, the sequence of observation as a function of increasing fluence is as follows.

i) Both in orthorhombic and monoclinic crystals, defect clusters are observed above fluences  $\sim 3 \times 10^{11}$  Kr/cm<sup>2</sup>. These clusters (or dislocations) interact immediately with the twin boundaries: the moving and pinning of dislocations on the twin boundaries are observed on a video recording [23]. Above a fluence of  $\sim 5 \times 10^{11}$  Kr/cm<sup>2</sup> the trapping of defect clusters on the twin boundaries is observed. At higher fluences we observe inhomogeneous contrast and (at  $\sim 10^{12}$  Kr/cm<sup>2</sup>) the formation of separate clusters inside the twin boundaries. Defect cluster trapping and dislocation pinning on the twin boundaries thus lead to the deformation of the twin boundaries (see Figs. 3, 4). Detailed analyses of this process will be reported elsewhere [24]. These observations show that the defects created in a high damage cascade (i.e. with heavy ions) are very mobile (even at low temperature) when the irradiation level reaches the cascade overlapping regime.

At this stage of irradiation, no evidence of an orthorhombic to tetragonal transition was found in the Os phase and in Ms only an apparent deformation/rotation is observed.

ii) Above  $4 - 5 \times 10^{12}$  Kr/cm<sup>2</sup> the heavily damaged twin boundaries progressively disappear as diffuse rings characteristic of an amorphous structure appear and are progressively enhanced.

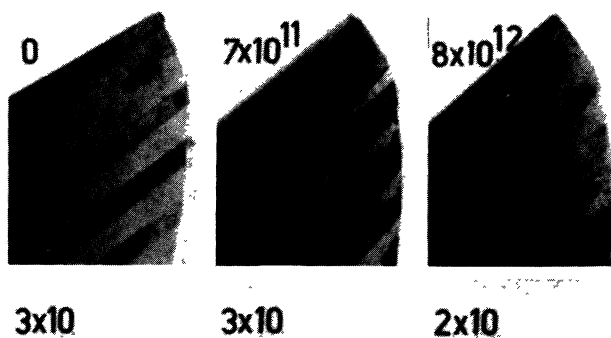


Fig. 3. — Bright fields of the same crystal as in figure 1 : defect evolution during 480 keV Kr ion irradiation at 40 K. Doses (Kr/cm<sup>2</sup>) are reported on the pictures.

At this stage a new apparent deformation/rotation occurred in the one Ms structure observed and finally we observed a Ms to tetragonal transition (above  $\sim 1.7 \times 10^{13}$  Kr/cm<sup>2</sup>). Occasionally the OTT transition also occurs in Os crystals.

### Discussion and conclusion.

i) From the above results we conclude that a deformation in the Cu-O basal plane of the orthorhombic structure leading to a monoclinic structure has no drastic influence on the structural evolution of the crystal during heavy ion irradiation. Whether or not this deformation has any influence on the superconducting properties is still an open question.

ii) Previous He ion irradiation studies led us to propose that at least two types of defects were involved in the structural changes observed during light ion irradiation. First, very mobile anionic defects associated with oxygen are responsible for the cluster formation at low temperature and for the OTT transition. Secondly less mobile cationic defects are related to amorphization [8]. For heavy ion irradiation OTT occurs at the same level of disorder as for light ion irradiation ( $\sim 0.1$  displacement per atom ratio : dpa). For reasons discussed in reference [8], it is univocally related to sublattice disordering. The results obtained here strongly indicate that there is no difference in the process leading to the OTT between light and heavy ion irradiation. The amorphization process is simply sufficiently efficient in the heavy ion irradiation case to partially mask the OTT.

iii) In the case of heavy ion irradiation, the amorphization occurs at fluences which are more than 3 orders of magnitude lower than for He irradiation (above  $4 - 5 \times 10^{12}$  Kr/cm<sup>2</sup> instead of  $\geq 10^{16}$  He/cm<sup>2</sup>). For heavy ion irradiation, the average energy transferred per collision is significantly larger so that cation displacements are definitely enhanced. Also the deposited energy density is about two orders of magnitude larger than in the light ion irradiation (according to TRIM calculation [25] the average numbers of displaced cations for He and Kr ion irradiation are respectively  $\sim 60$  and  $1600$ ).

iv) In order to analyze the amorphization process, the following question arises. For irradiation, could amorphous zones be created directly by the individual cascades so that amorphization would proceed by simple cascade overlap? From our results, we obtain the following information regarding this question.

1) The threshold fluence of amorphization is at least an order of magnitude higher than the threshold fluence for the cascade overlap ( $\sim 10^{10}$  Kr/cm<sup>2</sup>). This value does not take into account the heterogeneity of the 480 keV Kr ion

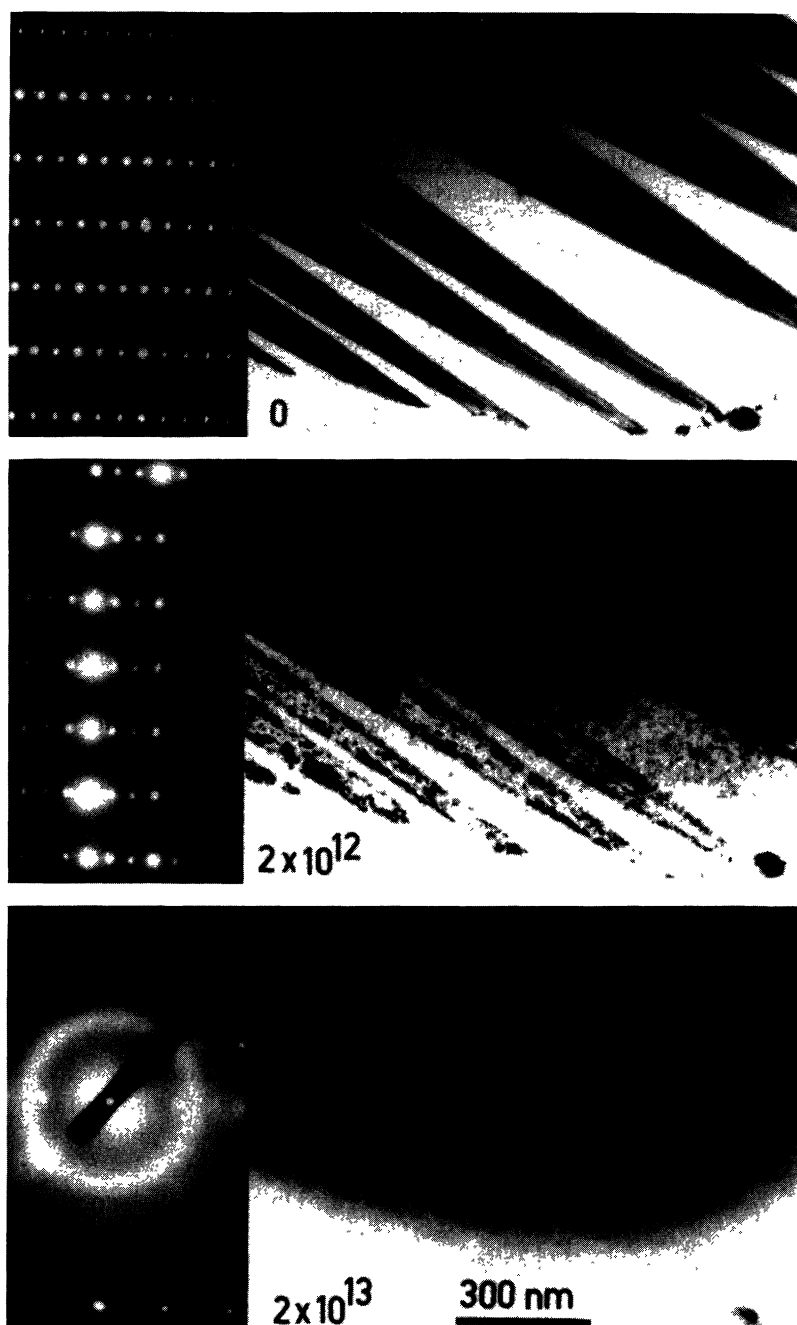


Fig. 4. — Defect evolution of an orthorhombic GdBaCuO crystal (with  $c$  axis parallel to the zone axis) irradiated at 300 K with 480 keV Kr ions.

cascades as we consider the overlap of the whole extension of the cascade (i.e. both light and high damage density zones) instead of only subcascade overlap (high damage density zones). This result indicates that amorphization does not proceed by the overlap of light damage density zones. However amorphous zones could be created directly inside subcascades (i.e. large damage density zones).

2) The clusters observed ( $> 10^{11}$  Kr/cm<sup>2</sup>) below the threshold fluence for subcascade overlap ( $\sim 5 \times$

$10^{11}$  Kr/cm<sup>2</sup>) are directly formed inside subcascades. However cluster interaction which leads to the formation of dislocations and their interaction with twin boundaries imply that the clusters involved in this interaction process do not have an amorphous structure.

3) Although most of the visible clusters are certainly not amorphous, they represent less than 10 % of the high density damaged zones created directly in the cascades. Whether or not visible clusters are

partially amorphous is still an unresolved question [23, 26], but in any case the amorphization is not induced by the overlap of visible amorphous clusters.

This leads us to propose that amorphized zones are created inside an individual cascade but are either relaxed or very small in size ( $< 2$  nm) and do not lead to visible strained amorphous clusters. The overlap of these amorphous zones induces amorphization. Therefore two types of extended defects are probably formed during heavy ion irradiation :

i) unresolved dislocation loops which leads to dislocation formation and interaction with twin boundaries ; ii) amorphous zones, presumably invisible by TEM, which induce amorphization.

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